ENERGETIC DISTRIBUTIONS OF OXYGEN SURFACE COMPLEXES ON POROUS CARBONS AND CHARS

P.J. Hall and J.M. Calo
Chemical Engineering Program
Division of Engineering
Brown University
Providence, Rhode Island 02912

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INTRODUCTION

When an oxidized coal char is subjected to a program of increasing temperature, the surface oxides desorb primarily as the oxides of carbon, CO and CO_2 (e.g., [1]). This process produces TPD spectra which can be interpreted in terms of the energetic state of chemisorbed surface complexes and interaction phenomena occurring within the char structure during the TPD process. The latter have been shown to be [2]: (1) the desorption of rechemisorbed CO released at lower temperatures, appearing primarily as a feature centered typically *ca.* 1200K; and (2) secondary CO_2 evolution which appears as a reflection or satellite peak under primary CO desorption features. We have attributed the latter to:

$$CO(g) + C(O) \Leftrightarrow C_f + CO_2(g) \qquad [R.1]$$

where: CO(g) represents "free," gaseous CO resulting from the desorption of a surface oxygen complex; C(O) is a surface oxygen complex; and C_f is an unoccupied surface active site.

From the perspective of previous work, including our own, there appear to be two principal obstacles to the direct application of TPD to the understanding of the behavior of oxygen surface complexes: (1) a more quantitative interpretation of the data; (2) deconvolution of secondary interactions from TPD spectra in order to enable the analysis of such data in terms of the energetics of the surface complexes. These issues are addressed in the current communication.

EXPERIMENTAL

Chars were prepared from Pittsburgh #8 and Wyodak coals obtained from the Argonne Premium Coal Sample Bank *via* pyrolysis in ultrahigh purity helium at 1273K with a soak time of 1 hour.

The TPD apparatus and methods have been described elsewhere [2]. The most salient experimental details are as follows. Char oxidation/gasification was performed in a TGA

apparatus in 0.1 MPa O_2 at the temperatures noted. Following cooling to room temperature in the TGA apparatus, the samples were transferred to a TPD reactor. Tests involving comparisons of TPD spectra obtained using this procedure with those following *in situ* oxidation in the TPD reactor have shown that transfer of the sample does not affect the resultant spectra.

The TPD reactor was constructed from a high-purity silica tube, 1-cm inside diameter, within which a close-fitting, circular silica sinter is used to support the sample. Ultrahigh purity helium carrier gas is passed over the sample in downflow. Heating is accomplished electrically via nichrome wire wrapped around the outside of the silica tube, powered by a high current variable transformer. The heating regimen is controlled by a microcomputer. The resultant TPD reactor has a low thermal capacitance which allows linear heating rates of up to 500K/min.

Detection of desorbed species is accomplished with a quadrupole mass spectrometer (MS) which samples a small portion of the carrier flow. The MS output is fed to a microcomputer which also provides for multiple species detection via mass programming.

Typical sample sizes for the TPD measurements were ~10 mg. This size resulted in less than a monolayer coverage on the silica frit that was used as the sample holder in the TPD reactor. This, when combined with high helium carrier gas sweep rates, insured the absence of secondary interactions between the bulk gas species and the char samples.

Repeated experiments with char samples obtained from the same batch indicate that the reproducibility of gas desorption rates is approximately ±10%. This error is attributable to a combination of effects arising primarily from sample inhomogeneity, sample size and MS calibration. For this reason, the spectra reported are representative, rather than averages.

RESULTS AND DISCUSSION

Deconvolution of TPD Spectra.

Over the course of examining many TPD spectra from oxygen-oxidized chars, it was noted that the leading edge of the *total oxygen* (i.e., $CO+2CO_2$) desorption feature centered *ca.* 1000K always seems to be reasonably well approximated by a Gaussian distribution. For this reason, it was decided to investigate the deconvolution of the total oxygen production rate into two contributions - one as a Gaussian centered at the maximum rate of production, with the variance determined from the leading edge of the 1000K peak, and the other as a higher temperature residual difference peak. The results of such a deconvolution for spectra obtained from an oxidized Wyodak coal char are presented in Figure 1. As shown, the Gaussian approximation is quite reasonable for describing the leading edge of the total oxygen distribution, and the residual peak appears to be relatively smaller and non-Gaussian.

As it stands, such a deconvolution is nonunique, and thus we are faced with the question of whether the high temperature end of the 1000K oxygen peak remains near-Gaussian in the region

where it cannot be directly observed. There is some experimental evidence in support of this hypothesis.

One such piece of evidence is provided by a set of previously reported experiments with Wyodak coal char [3] in a slightly different context, and re-analyzed here. The coal char was gasified to 15.2% burn-off (in 0.1MPa oxygen at 623K) in the TGA apparatus. In the current analysis only the CO data are analyzed, although similar results were found for total oxygen spectra as well, due to the relatively minor contribution of the CO_2 in this case. A sample of the gasified char was *partially cleaned* by heating to 1100K at 100K/min, and was then quickly cooled (at a rate exceeding 200K/min) in ultrahigh purity helium. This was done not only to remove complexes stable below 1000K, but also as an attempt to effectively "titrate" the high temperature sites suspected of involvement in CO re-adsorption that give rise to the 1200K peak in TPD spectra. A second sample of the same coal char, oxidized under the same conditions, was subjected to TPD to 1100K and quick cooling in He to room temperature. Then, a TPD was carried out to 1400K. The result of this experiment is the "high temperature - clean" CO spectrum [HT] presented in Figure 2. The "partially cleaned" sample, with high temperature CO remaining on the surface, was then re-oxidized in the TPD apparatus under non-gasifying conditions in 0.1MPa of oxygen at 473K for 12 hours. We have shown that this treatment effectively reoxidizes practically all the surface sites created during the original gasification for the Wyodak coal char [3]. TPD was then carried out on this partially cleaned and reoxidized char, and this result is designated as the [PC] spectrum in Figure 2. The difference between the "high temperature - clean" TPD [HT] and the "partially cleaned/reoxidized" TPD [PC] then represents the surface oxygen added during reoxidation. This is designated as [HT-PC] in Figure 2. From the arguments presented above, this difference spectrum should be uncomplicated by CO re-chemisorption, and the resultant distribution should, therefore, be reflective of the original state of the oxygen chemisorbed during reoxidation. As shown in the figure, a Gaussian distribution seems to fit the difference spectrum reasonably well. This agreement suggests that the *intrinsic* 1000K peak for oxygen production may indeed be Gaussian over its entire range.

Energetic Distributions.

In view of the available evidence in support of a Gaussian distribution for the 1000K feature, the question naturally arises as to what the physical basis may be for this type of distribution. In considering this question, it is useful to transform the TPD spectra from a temperature to a desorption energy basis, using a procedure derived from the original work of Redhead [4]. A brief outline of the derivation follows.

For a *continuous* distribution of *i* species on a *heterogeneous* surface, each obeying a first order desorption rate law characterized by a single desorption activation energy, E_i, there must also be a *continuous* distribution of maximum desorption temperatures, $T_{p,i}$, one for each of the *i* species. These are related to the E_i *via* a familiar expression derived by Redhead [4]. Since the relationship between desorption activation energy and temperature is very nearly linear over

a large range of parameter values, this is closely approximated by the expression:

$$E_i/RT_{p,i} = \ln [\nu_o T_{p,i}/\beta] - 3.64, \quad [1]$$

which for $10^{13} > \nu_i/\beta > 10^8$ (K^{-1}), was shown to be accurate to within $\pm$ 1.5% [4].

If the $T_{p,i}$ are described by a continuous probability density function, then each instantaneous temperature, T, during a heating regimen must also correspond to some $T_{p,i}$. As a consequence, an expression like Eq. [1] provides a direct transformation between the observed experimental desorption temperature, T, and the desorption activation energy distribution, $S(E_i)$. Furthermore, since Eq.[1] is evaluated at the peak temperature, $T_{p,i}$, then the heating rate, β, is rigorously defined as the local *instantaneous* heating rate at $T_{p,i}$, or, more generally, at temperature T. Therefore, Eq. [1] applies to a first order desorption process for any monotonic heating regimen exhibiting a maximum in desorption rate.

An analysis of the continuity expression for surface oxygen complexes can be shown to yield the following expression for the total desorption rate of CO from the surface:In this expression,

$$d[CO]/dt = [C\text{-}O]_o \, S(E^*) \, dE^*/dt \quad [2]$$

where $[C\text{-}O]_o$ is the total amount of oxygen surface complex initially on the char surface, $S(E^*)$ is the probability density function of desorption activation energies, and dE^*/dt is the time derivative of the desorption activation energy during the heating regimen. In deriving this expression, the resultant integral over the distributed desorption rate constant was approximated as a step function occurring at a critical activation energy, E^* (*cf.* [5,6]), since it increases over a very narrow energy range from zero to unity. Since a TPD experiment yields the instantaneous d[CO]/dt directly, then knowledge of E^* and dE^*/dt defines the initial energetic distribution of surface complex, $[C\text{-}O]_o S(E^*)$, experimentally. Differentiating Eq. [1]:

$$dE^*/dt = R\beta \, [E^*/RT] = R\beta \, [\ln (\nu_o T/\beta) - 3.64]. \quad [3]$$

Combining Eqns. [2] and [3], then yields the energetic distribution of surface complexes as:

$$[C\text{-}O]_o S(E^*) = \{d[CO]/dt\}/\{R\beta \, [\ln (\nu_o T/\beta) - 3.64]\}. \quad [4]$$

From this expression, the energetic distribution of oxygen surface complexes can be determined experimentally from TPD spectra. Eq. [4] indicates that this transformation is practically linear for constant heating rate, β; i.e., the logarithmic term does not vary appreciably over the TPD temperature range. Thus, for *linear* TPD, if the distribution of the surface complex desorption in temperature is Gaussian, then the distribution of desorption activation energies will be close to

Gaussian as well.

One interpretation of a Gaussian energetic distribution is that the oxygen surface complexes exhibit a continuum, random distribution of binding energies. For many typical coal chars, most of the surface area and, consequently, most of the oxygen complexes, are present in micropores. In these small pores of molecular dimensions, the effective binding energies of the complexes would be strongly influenced by the local environment, the presence of neighboring complexes etc., and thus may be randomly distributed. For example, an oxygen atom could be bound to opposing walls of a micropore (e.g., an ether linkage). The binding energy of such a complex would vary according to the local width of the micropore, and, ultimately, in a very wide micropore, or a mesopore, the complex could be bound to only one wall, thereby assuming a semiquinone or carbonyl character. In other words, oxygen functional groups that may otherwise be chemically distinct on an "open" surface, may ultimately "blend" into one another in a multi-surface environment of molecular dimensions, as in micropores.

This *rationale* for a Gaussian distribution of desorption activation energies suggests that the resultant energetic distribution should be a characteristic property of the char and its porosity, and *not* a function of heating rate. In order words, once the distribution of desorption activation energies is known, it should enable the prediction of desorption spectra obtained under any heating regimen. In addition, the fact that it is the *total oxygen* distribution that appears to be Gaussian supports the hypothesis that the secondary interaction features arise primarily from the same source as the "1000K CO." These points are demonstrated below using TPD data obtained from Pittsburgh #8 coal char.

In Figure 3 is presented a 100K/min total oxygen TPD spectrum from a sample of Pittsburgh #8 coal char gasified to 10% burn-off at 723K in 0.1MPa of O_2, along with a Gaussian fit to the leading edge of the principal desorption feature. As discussed above, the high temperature peak/shoulder is believed to originate primarily from CO originally liberated during desorption of the 1000K oxygen complexes and re-chemisorbed to be liberated once again as "1200K CO." Therefore, in order to be consistent in reconstructing the original state of the oxygen complex distribution on the char surface, the additional oxygen represented by the difference between the integral over the total oxygen desorption and the Gaussian fit to the 1000K peak should be added to the latter to yield a "corrected" Gaussian, as shown in Figure 3. For example, for the Pittsburgh #8 coal char sample this amounted to an amplitude correction (increase) of 20%.

The "corrected" Gaussian distribution was then transformed into an energetic distribution using Eq. [4]. As indicated above, for a linear heating rate, the transformation between the TPD spectrum with respect to temperature and the energetic distribution is practically linear, so that the resultant S(E*) distribution is also quite close to Gaussian as well. The construction of this distribution requires the assumption of values for the pre-exponential frequency factor, ν_o. Originally we tried using ν_o=kT/h, the frequency factor predicted by transition state theory.

However, this did not result in the best fits to total oxygen TPD spectra obtained at different heating rates for the same char. In any case, these values are simply estimates. Therefore, it was decided to vary ν_o in such a manner as to obtain the best fit to TPD spectra obtained at the nominal heating rates of 20, 100, and 300K/min. The calculations were, therefore, iterative, and were performed using a spreadsheet program. Essentially, the procedure involved assuming a value of ν_o to obtain an energetic distribution from the 100K/min data. This distribution was then used to predict the 20 and 300K/min total oxygen TPD spectra, "corrected" for rechemisorbed oxygen as described above. The final energetic distribution, arrived at in this manner, was approximately Gaussian with a mean of 48.8 kcal/mol and a standard deviation of 6.9 kcal/mol. The total amount of surface oxygen was 2.4 mmol/g. A value of $\nu_o = 10^{11}$ min^{-1} yielded the best predictions, although reasonable results were also obtained over a range of ν_o of about an order of magnitude in either direction, so this value is not necessarily unique. A summary of the final TPD curves, predicted from the energetic distribution, for the three heating rates used, along with the corresponding "corrected" data, are presented in Figure 4.

CONCLUSIONS

Based on these results, it is concluded that Gaussian deconvolution of the 1000K peak from total oxygen TPD spectra seems to be a reasonable approximation. The amount of rechemisorbed CO may be estimated using this procedure. The resultant Gaussian spectra can be transformed to obtain the probability density distribution function of desorption activation energies which is related to the energetic state of oxygen complexes on coal char surfaces. This distribution is a characteristic property of the char and can be used for kinetic predictions involving the thermal desorption rates of such complexes, and/or as a diagnostic of the nature of the active sites.

The authors believe that the quantitative description of char surfaces *via* energetic distributions represents a new and more fundamental approach to all issues related to char reactivity. It is anticipated that techniques arising from such descriptions will eventually supplant more empirical methods.

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REFERENCES

1. Tremblay, G.; Vastola, F.J.; Walker, P.L., Jr., *Carbon* **1978,** *16,* 35.
2. Hall, P.J.; Calo, J.M., *Energy & Fuels* **1989,** *3,* 370.
3. Hall, P.J.; Calo, J.M.; and Otake *Proc. Nineteenth Biennial Conf. Carbon,* **1989,** p. 594.
4. Redhead, P.A. *Vacuum* **1962,** *12,* 203.
5. Suuberg, E.M. , *Comb. Flame* **1983,** *50,* 243.
6. Du, Z., Sarofim, A.F., and Longwell, J.P. *Energy & Fuels* **1990,** in press.

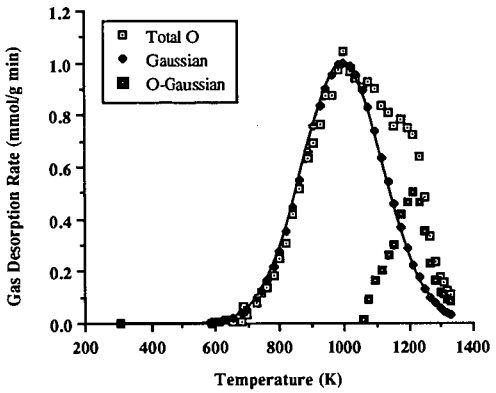

Figure 1. Deconvolution of 100K/min total oxygen TPD spectra from Wyodak coal char gasified to 15.2% burn-off in 0.1MPa of O_2 at 350°C into a Gaussian and a residual.

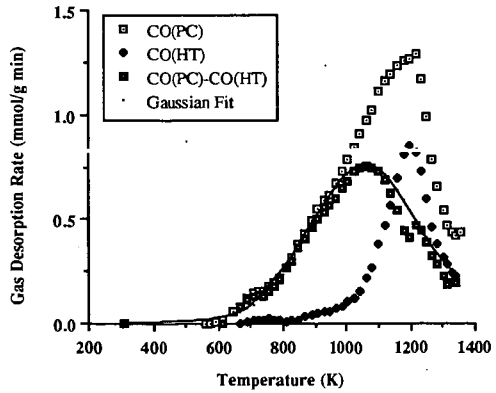

Figure 2. 100K/min CO TPD spectra from Wyodak coal char, originally burned-off to 15.2% in 0.1MPa O_2. CO(PC): after partial cleaning to 1100K and re-oxidation in 0.1MPa O_2 at 200°C for 12h; CO(HT): residual high temperature surface complexes after partial cleaning to 1100K; CO(PC)-CO(HT): difference spectrum.

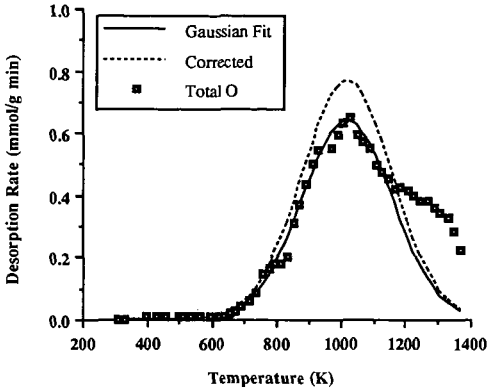

Figure 3. 100K/min total oxygen TPD spectrum from Pittsburgh #8 coal char gasified to 10% burn-off in 0.1MPa of O_2 at 723K, and Gaussian fits; both direct and "corrected."

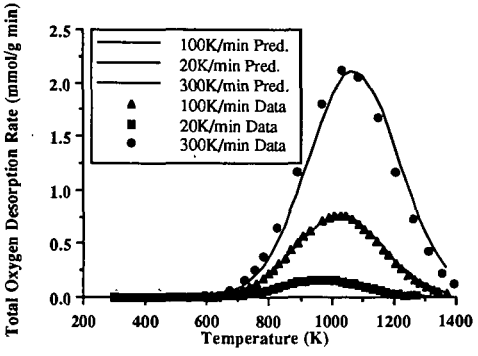

Figure 4. Total oxygen TPD spectra as a function of linear heating rate for Pittsburgh #8 coal char burned-off to 10% in 0.1MPa O_2 at 723K; both "corrected" data and predictions.